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# EUROPEAN PATENT OFFICE

## Patent Abstracts of Japan

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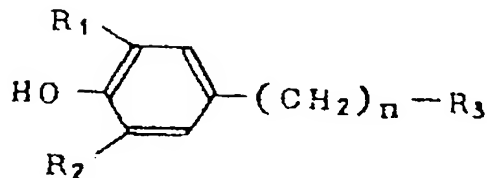
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APPLICANT : TORAY IND INC;

INVENTOR : OKASAKA HIDESADA;

INT.CL. : C08G 63/22

TITLE : PRODUCTION OF POLYESTER



ABSTRACT : PURPOSE: To produce a polyester which can form a film excellent in transparency, flatness, slidability and electrical properties, by adding a phosphorous compound and a specified amount of fine particles to the reaction mixture during polycondensation reaction.

CONSTITUTION: In the production of a polyester consisting mainly of repeating units of ethylene terephthalate, 0.05~5wt% phosphorus compound of a MW  $\geq 300$  and 0.005~2wt% fine particles of an average particle diameter of 0.03~3 $\mu$ m are added to the reaction mixture during the reaction from the time before the start of esterification or transesterification to the time of completion of polycondensation reaction. As the phosphorus compounds, those containing a phenolic hydroxyl group of the formula (wherein R<sub>1</sub> and R<sub>2</sub> are each a 1~10C alkyl, R<sub>3</sub> is a 2~24C phosphinate or phosphonate group and n is 0~5) are desirable. As said fine particles, those of e.g., calcium carbonate, silicon dioxide, etc., are used.

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## SPECIFICATION

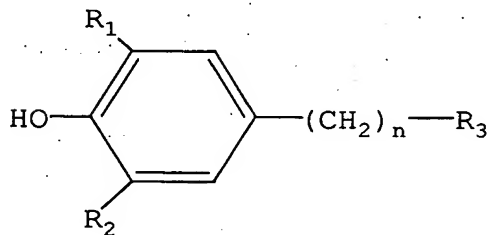
### 1. Title of the invention

#### PROCESS FOR PREPARING POLYESTER

### 2. Claims

(1) A process for preparing polyester, which comprises adding 0.05 to 5.0% by weight of a phosphorus compound having a molecular weight of 300 or larger and 0.005 to 2.0% by weight of a fine particle having an average particle diameter of 0.03 to 3.0  $\mu$  from before initiation of esterification or transesterification reaction to completion of a polycondensation reaction, upon preparation of polyester having a main repetition unit of ethylene terephthalate.

(2) The process for preparing polyester according to claim (1), wherein the phosphorus is a phenolic hydroxy group-containing phosphorus compound represented by the following general formula:



(wherein n is an integer of 0 to 2, R<sub>1</sub> and R<sub>2</sub> are hydrogen or an alkyl group having a carbon number of 1 to 10, and R<sub>3</sub> is a phosphinic acid ester group or a phosphonic acid ester group)

having a carbon number of 2 to 24.

### 3. Detailed explanation of the invention

#### [Technical field]

The present invention relates to a process for preparing polyester containing a specified phosphorus compound and a fine particle at a specified amount, in particular, a film forming polyester excellent in the transparency, the flatness, the sliding property and the electric property.

#### [Prior art and problems thereof]

Recently, a polyethylene terephthalate film has been remarkably progressed into the fields of a magnetic tape, a photograph, a condenser, a package and a microfilm.

In order to improve the transparency of the previous film, various methods have been proposed. However, since all of these methods emphasize on the transparency, the resulting film has the defect that it is remarkably inferior in the easy sliding property.

Among the required properties, in particular, impartation of the easy sliding property is important. When the surface is not easily sliding, phenomenon of adhesion between films occurs, not only working performance is reduced at film making or post-processing, but also winding appearance is deteriorated. Therefore, there is caused a problem that

product value is remarkably reduced.

On the other hand, when used as a magnetic recording medium for magnetic tape utility, it is required that a film has small surface irregularity and is excellent in so-called flatness, and is excellent in the sliding property, in order to prevent reduction in output and drop out.

In addition, also in condenser film utility, it is required that a film has both of the electric property and the sliding property which conflict with each other.

In order to solve these problems, many techniques have previously been proposed and practiced. They are roughly classified into a method of adding a fine particle which is inert to a polyester synthesis reaction system such as titanium dioxide, talc, kaolinite, calcium carbonate and silicon oxide, and a method of precipitating a part or all of a catalyst and a coloring preventing agent used at polyester synthesis during a reaction to make them exist as a fine particle.

However, the film obtained by these methods can not obtain the sufficient grinding property in the state where it maintains the flatness.

For example, JP-A No. 55-21157 gazette having an object of improving the electric property and the grinding property of a condenser film is known. This is a polyester film obtained by performing a transesterification reaction of polyester in the presence of a calcium compound, adding a phosphorus compound

at 1 to 2-fold mol relative to a calcium compound, and adding a specified inert particle. However, this film has the defect that when an inert particle is added in order to impart the sufficient grinding property, the better electric property is hardly obtained.

On the other hand, JP-B.No. 34-5144 gazette discloses a method of using a trivalent phosphorus compound jointly. In this case, a particle of an alkaline earth metal salt of terephthalic acid is rather reduced, and the resulting film is excellent in the transparency, the flatness and the electric property, but lacks the sliding property, and has a problem that blocking occurs in a winding step.

[Object of the invention]

An object of the present invention is to provide a process for preparing film forming polyester having all of the transparency, the flatness, the sliding property and the electric property which could not be attained in the prior art.

[Essential features of the invention]

The aforementioned object of the present invention can be attained by (1) a process for preparing polyester, which comprises adding 0.05 to 5.0% by weight of a phosphorus compound having a molecular weight of 300 or larger and 0.005 to 2.0% by weight of a fine particle having an average particle diameter

of 0.03 to 3.0  $\mu$  from before initiation of esterification or transesterification reaction to completion of a polycondensation reaction, upon preparation of polyester having a main repetition unit of ethylene terephthalate.

Then, the present invention will be explained in detail. The polyester of the present invention contains mainly polyethylene terephthalate, which can be molded into a fiber, a film or other molded articles, and can be prepared by the previously known various methods. Of course, these polyesters may be homopolyester or copolyester. Examples of a component to be copolymerized include a diol component such as diethylene glycol, propylene glycol, neopentyl glycol, polyalkylene glycol, p-xylene glycol, 1,4-cyclohexanedimethanol, and 5-sodiumsulforesorcine, a dicarboxylic acid component such as adipic acid, sebacic acid, phthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, and 5-sodiumsulfoisophthalic acid, a multifunctional dicarboxylic acid component such as trimellitic acid and pyromellitic acid, and an oxycarboxylic acid component such as p-oxyethoxybenzoic acid.

After an esterification reaction with glycol when a dicarboxylic acid component is dicarboxylic acid, or after a transesterification reaction with glycol when a dicarboxylic acid component is dicarboxylic acid ester, polycondensation is performed at a high temperature under reduced pressure to obtain

polyester.

Alternatively, polycondensation may be performed using a prepolymer itself as a starting material.

A fine particle having an average particle diameter of not smaller than  $0.05\ \mu$  and not larger than  $3.0\ \mu$  in the present invention refers to an inert particle described below, and examples of a kind thereof include fine powders of calcium carbonate, wet silicon oxide, dry silicon oxide, aluminium silicate, barium sulfate, calcium phosphate, talc, titanium dioxide, aluminium oxide, aluminium hydroxide, calcium terephthalate, calcium silicate, fluorine-containing series fine particle polymer and cross-linked polymer which are obtained as a synthetic or natural product. An amount of these fine particles to be added is 0.005 to 2.0% by weight, preferably 0.005 to 1.0% by weight, further preferably 0.01 to 0.5% by weight. When a content of a particle is smaller than 0.005% by weight, a friction coefficient between films, or film and metal becomes larger when formed into a film. On the other hand, when a content of a particle exceeds 2.0% by weight, occurrence of a coarse particle is increased, the flatness when formed into a film is inhibited, and since a coarse particle becomes a starting point of dielectric breakdown, dielectric breakdown voltage property is remarkably reduced, and there may be adverse influence on choking of a filter during melt molding and film rupture, being not preferable.



In addition, in order to balance the flatness, the transparency and the electric property of the film surface, it is necessary that an average particle diameter of a fine particle is 0.03 to 3.0  $\mu$ , and a more preferable particle average particle diameter range is 0.1 to 2.0  $\mu$ .

When the polyester of the present invention is formed into a film, if an average diameter of a particle is smaller than 0.03  $\mu$ , the sliding property of a film is reduced.

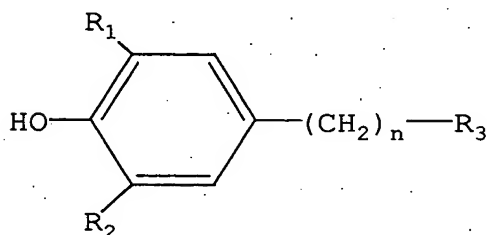
On the other hand, when an average diameter exceeds 3.0  $\mu$ , the dielectric breakdown voltage property is reduced due to a coarse particle, and the flatness of a film is reduced.

In order to remove a coarse particle from these fine particles and adjust a particle size of those particles, various methods which are usually used, for example, air elutriation classification, spontaneous settlement separation using ethylene glycol slurry or aqueous slurry, centrifugation settlement separation, grinding with a sand mill and/or classification treatment may be adopted.

Examples of a phosphorus compound having a molecular weight of 300 or larger, preferably 400 or larger in the present invention include sec-butylidenetriphenylphosphorane, benzylidenetriphenylphosphorane, phenyldiisooctyl phosphite, diisodecylpentaerythritol diphosphite, tricyclohexyl phosphate, and tri-p-toluyyl phosphate.

Among them, a phenolic hydroxy group-containing

phosphorus compound having a molecular weight of 400 or larger represented by the following general formula is particularly preferable in that it considerably improves the best easy sliding property and the electric property such as dielectric breakdown voltage.



(wherein  $n$  is an integer of 0 to 5,  $R_1$  and  $R_2$  are hydrogen or an alkyl group having a carbon number of 1 to 10, and  $R_3$  is a phosphinic acid ester group or a phosphonic acid ester group having a carbon number of 2 to 24)

When a molecular weight of these phosphorus compounds is smaller than 300, if an addition amount is smaller than 0.05 % by weight, the effect of the sliding property and the electric property such as dielectric breakdown voltage can not be obtained when formed into a polyester film. On the other hand, if an addition amount is larger than 5.0% by weight, polymerization productivity is deteriorated, being not preferable. For this reason, an amount of a phosphorus compound to be added is desirably 0.05 to 5.0% by weight, particularly preferably 0.05 to 3.0% by weight relative to polyester.

The polyester of the present invention may be used as it is, or may be used as a master polymer. In order to obtain the

aforementioned properties when formed into a polyester film, it is desirable that the polyester film contains a phosphorus element at 0.005 to 0.1% by weight. For this reason, a phosphorus compound can be appropriately used so that a content of a phosphorus element in the film is in the aforementioned range. When a phosphorus element in the film exceeds 0.1% by weight, this causes reduction in a film making rate, being not preferable.

A fine particle and a phosphorus compound may be added before a reaction of polymerizing polyester, during a polymerization reaction, or after completion of a polymerization reaction. It is preferable that a fine particle is added as a slurry dispersed in water and/or ethylene glycol before a polymerization reaction or during a reaction.

[Effect of the invention]

As the characteristic of a film prepared using the polyester of the invention, since the film contains a fine particle having a specified particle diameter at a specified amount and a phosphorus compound having a specified molecular weight at a specified amount, the following excellent effects are exerted.

(1) Choking of a filter is less frequent during melt molding of a film, and rupture of a film membrane due to a coarse particle is less frequent.

(2) Since the film surface is excellent in the flatness, there is no defects such as drop out and sound skipping at regeneration in magnetic tape utility, being extremely useful.

(3) Since the film has a better friction coefficient, it is excellent in the step passing property and the handling property.

(4) The film is excellent in the electric property such as dielectric breakdown voltage.

As described above, the polyester composition of the present invention can be preferably used as an unstretched film and a stretched film.

The present invention will be explained in detailed below by way of Examples.

Each property value of the polyesters in Examples was measured by the following method.

(Particle diameter)

An average particle diameter was obtained by an equivalent sphere diameter of a particle corresponding to 50% by weight measured by a light microscope photograph or an electron microscope photograph of a particle. An equivalent sphere diameter is a diameter of a sphere having the same volume as that of a particle.

(Film haze)

A film haze was measured according to ASTM-D-1003-52.  
(Friction coefficient)

A friction coefficient was measured using a slip tester according to the ASTM-D-1894B method.

(Film surface roughness)

The film surface was observed according to a method prescribed in JIS-B0601 with a feeler roughness gauge, and maximum roughness and average roughness ( $\mu$ ) were obtained.

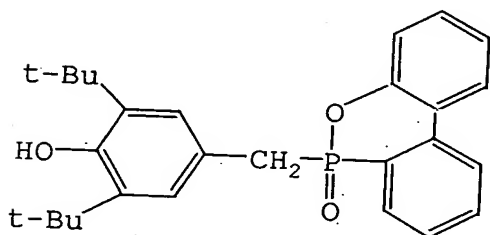
(Dielectric breakdown voltage)

A dielectric breakdown voltage was measured using an alternating current pressure resistant tester according to JIS-C-2316.

#### Example 1

100% by weight of dimethyl terephthalate, 65% by weight of ethylene glycol, 0.09% by weight of calcium acetate as a transesterification catalyst, and 0.03% by weight of antimony trichloride as a polymerization catalyst were added, and an approximately theoretical amount of methanol was distilled out at between 140 and 220°C to complete a transesterification reaction. Subsequently, 0.04% by weight of trimethyl phosphate, and 0.3% by weight of dry silica ( $\text{SiO}_2$ ) (manufactured by Nippon Aerosil Co., Ltd., "Aerosil"R-972) were added as an ethylene glycol slurry to the system. Subsequently, the system was gradually evacuated, ethylene glycol was distilled off

under reduced pressure of 1mmHg or lower at a temperature of 285°C, and the reaction was completed in 4 hours. After completion of the reaction, 1.0% by weight of a phenolic hydroxy group-containing phosphorus compound (hereinafter, abbreviated as PIR) having the following structure was added, and kneading was performed under reduced pressure for about 10 minutes to obtain a polymer having an intrinsic viscosity of 2.612 containing 0.3% by weight of SiO<sub>2</sub>.



The thus obtained polyester was dried under reduced pressure (170°C × 2 hours), melt-extruded at 285°C, and cast on a cooling drum at 60°C to obtain an unstretched sheet, which was stretched at 3.3-fold in a longitudinal direction and 3.5-fold in a transverse direction by the conventional method, and heat-treated at 215°C while slightly relaxing to obtain a polyethylene terephthalate biaxially stretched film having a thickness of 5 μ. The resulting film had a haze of 1.9%, a static friction coefficient of 0.60, average roughness of the film surface of 0.020 μ, film surface maximum roughness of 0.20 μ and a dielectric breakdown voltage of 548 v/μ, thus, was extremely excellent in all of the transparency, the flatness, the sliding property and the electric property.

## Example 2

100% by weight of dimethyl terephthalate, 65% by weight of ethylene glycol, 0.09% by weight of calcium acetate as a transesterification catalyst, and 0.03% by weight of antimony trioxide as a polymerization catalyst were added, and an approximately theoretical amount of methanol was distilled out at between 140 and 220°C to complete a transesterification reaction. Subsequently, 0.04% by weight of trimethyl phosphate and 1.0% by weight of dry silica ( $\text{SiO}_2$ ) (manufactured by Nippon Aerosil Co., Ltd., "Aerosil" R-972) having an average particle diameter of 0.3  $\mu$  were added as an ethylene glycol slurry to the system. Subsequently, the system was gradually evacuated, ethylene glycol was distilled off under reduced pressure of 1mmHg or lower at 285°C, and the reaction was completed in 4 hours. The resulting polymer had an intrinsic viscosity of 0.618, and contained 1.0% by weight of  $\text{SiO}_2$ .  
(Polyester: A)

According to the same manner as that for Polyester:A, a polymer having an intrinsic viscosity of 0.61 to which no inert particle was added, was obtained. (Polyester: B)

100% by weight of dimethyl terephthalate, 65% by weight of ethylene glycol, 0.09% by weight of calcium acetate as a transesterification catalyst, and 0.03% by weight of antimony trioxide as a polymerization catalyst were added, and a

theoretical amount of methanol was distilled out at between 450 to 220°C to complete a transesterification reaction.

Subsequently, 0.1% by weight of dimethylphenyl phosphonate and 0.03% by weight of phosphorous acid were added, a polycondensation reaction was performed according to the conventional method and, after completion of the reaction, 2.0% by weight of PIR was added, and kneading was performed under reduced pressure for about 10 minutes to obtain a polymer having an intrinsic viscosity of 0.609. (Polyester: C)

The thus obtained Polyester A, Polyester B and Polyester C were dried under reduced pressure (170°C × 2 hours) while mixing, and a composition comprising 100% by weight of polyester, 0.3% by weight of dry silica and 0.05% by weight (phosphorus amount) of PIR as a whole was obtained. The composition was melt-extruded at 285°C, and cast on a cooling drum at 60°C to obtain an unstretched sheet, which was stretched at 3.3-fold in a longitudinal direction and 3.5-fold in a transverse direction according to the conventional method, and heat-treated at 215°C while slightly relaxing to obtain a polyethylene terephthalate biaxially stretched film having a thickness of 5  $\mu$ . The resulting film had a haze of 2.0%, a static friction coefficient of 0.63, average roughness of the film surface of 0.018  $\mu$ , film surface maximum roughness of 0.20  $\mu$  and a dielectric breakdown voltage of 545 V/ $\mu$ , thus, was extremely excellent in all of the transparency, the flatness,



the sliding property and the electric property.

Example 3 (Experimental Examples 1 to 12)

According to the same manner as that for Polyester A of Example 2, polyester containing calcium carbonate having an average particle diameter of  $1.5\ \mu$  at 2.0% by weight relative to 100% by weight of polyethylene terephthalate in place of dry silica was obtained. (Polyester: D)

On the other hand, polyester having an average particle diameter of  $0.9\ \mu$  and containing 3.0% by weight of kaolinite was obtained. (Polyester: E)

These polymers and the polymer obtained in Example 2 as well as various phosphorus compound-containing polymers were blended, respectively, and a film as compositions shown in Experimental Examples 1 to 12 was prepared according to the same manner as that of Example 2. (Table-1)

Experimental Example 1 is inferior in the sliding property and the dielectric breakdown voltage, and Experimental Example 7 has an addition amount of kaolinite exceeding an upper limit, therefore, is inferior in the flatness and the dielectric breakdown voltage.

Since Experimental Examples 4 and 6 have no inert particle added, the sliding property is considerably reduced.

Experimental Examples 3 and 11 are an example in which a phosphorus amount of a phosphorus compound added in a film

and a molecular weight of a phosphorus compound are not preferable, and both of or either of the properties of the sliding property and dielectric breakdown voltage was (were) reduced.

Experimental Examples 2, 5, 8, 9, 10 and 12 are within the present invention, and were excellent in the sliding property, the flatness, and the dielectric breakdown voltage property.

Table 1

| Experimental Example | Composition  |      |        |                                  |                  |                   |      | Static friction coefficient | Film surface roughness (μ) |     | Film haze (%) | Dielectric breakdown voltage |
|----------------------|--|------|--------|----------------------------------|------------------|-------------------|------|-----------------------------|----------------------------|-----|---------------|------------------------------|
|                      | (%by weight relative to 100% by weight of polyester) |      |        |                                  |                  |                   |      |                             |                            |     |               |                              |
|                      | Phosphorus compound                                  |      |        |                                  |                  |                   |      |                             |                            |     |               |                              |
|                      | Inert particle                                       | Kind | Amount | Kind                             | Molecular weight | Phosphorus amount |      |                             |                            |     |               |                              |
| (Example 1)          | Dry silica   |      | 0.3    | PIR                              | 434              | 0.07              | 0.60 | 0.20                        | 0.020                      | 1.9 | 548           |                              |
| (Example 2)          | Dry silica   |      | 0.3    | PIR                              | 434              | 0.05              | 0.63 | 0.20                        | 0.018                      | 2.0 | 545           |                              |
| (Example 3) 1        | Dry silica   |      | 0.3    | -                                | -                | -                 | 0.85 | 0.23                        | 0.020                      | 1.8 | 465           |                              |
| 2                    | CaCO <sub>3</sub>                                    |      | 0.1    | PIR                              | 434              | 0.01              | 0.72 | 0.30                        | 0.028                      | 2.8 | 535           |                              |
| 3                    | Kaolinite  |      | 0.1    | PIR                              | 434              | 0.2               | 0.68 | 0.27                        | 0.025                      | 2.7 | 482           |                              |
| 4                    | -  |      | -      | PIR                              | 434              | 00.5              | 5.5  | 0.09                        | 0.012                      | 0.5 | 540           |                              |
| 5                    | Dry silica   |      | 0.5    | PIR                              | 434              | 0.01              | 0.52 | 0.25                        | 0.022                      | 2.5 | 534           |                              |
| 6                    | -  |      | -      | -                                | -                | -                 | 4.01 | 0.05                        | 0.009                      | 0.3 | 550           |                              |
| 7                    | Kaolinite  |      | 3.0    | PIR                              | 434              | 0.01              | 0.39 | 0.35                        | 0.040                      | 1.9 | 443           |                              |
| 8                    | Dry silica   |      | 0.3    | Phenyldiisooctyl phosphite       | 582              | 0.01              | 0.65 | 0.25                        | 0.025                      | 2.1 | 530           |                              |
| 9                    | Dry silica   |      | 0.3    | Tricyclohexyl phosphate          | 344              | 0.01              | 0.70 | 0.27                        | 0.026                      | 2.0 | 521           |                              |
| 10                   | Dry silica   |      | 0.3    | Benzylidene triphenylphospharane | 552              | 0.01              | 0.74 | 0.26                        | 0.024                      | 1.9 | 314           |                              |
| 11                   | Kaolinite  |      | 0.1    | Diphenyl phosphite               | 234              | 0.03              | 0.80 | 0.28                        | 0.025                      | 2.5 | 470           |                              |
| 12                   | Kaolinite  |      | 0.1    | PIR                              | 434              | 0.01              | 0.71 | 0.27                        | 0.026                      | 2.5 | 531           |                              |